

Fabrication and Characterization of Black GaAs Nanoarrays via ICP Etching

Jing Ma

Jihua Laboratory <https://orcid.org/0000-0003-1226-9210>

Yongqiang Zhao

Institute of Semiconductors Chinese Academy of Sciences

Wen Liu

institute of semiconductors, Chinese Academy of Science

Fuhua Yang

Institute of Semiconductors Chinese Academy of Sciences

Xiaodong Wang (✉ xdwang@semi.ac.cn)

Engineering Research Center for Semiconductor Integrated Technology, Institute of Semiconductors, Chinese Academy of Science, Beijing 100083, China <https://orcid.org/0000-0003-0426-1358>

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Abstract

GaAs nanostructures has attracted more and more attention due to its excellent properties such as increasing photon absorption. The fabrication process on GaAs substrate were rarely reported and most of the preparation processes are complex. Here, we reported a black GaAs fabrication process using a simple Inductively coupled plasma (ICP) etching process with no extra lithography process. The fabricated sample has a low Reflectance value close to zero. Besides, the black GaAs also displayed hydrophobic property, with a water contact angle (CA) of 125°. This kind of black GaAs etching process could be added to the fabrication workflow of photodetectors and solar cell devices to further improve their characteristics.

Introduction

Owing to its unique optical properties, light trapping structure plays a more and more important role in photovoltaic devices[1]. At present, researchers have developed all kinds of nanostructures as light trapping structures to increase light absorption in photovoltaics while most of them were performed on Si substrate[2–6]. III–V compound semiconductor nanostructures have been shown to be promising materials for a variety of optoelectronic and energy related applications such as light emitting diodes (LEDs)[7, 8], photovoltaics (PV)[9–12] and field effect transistors (FETs)[13–16]. GaAs is a promising candidate as its direct bandgap and absorption property[17, 18]. When incident light enters the nanostructure, the photons will undergo multiple reflections and refracts inside the structure and get trapped in the array, which is the trapping effect of nanostructure. And because of the absorption characteristics of GaAs materials, it means that more photon energy is absorbed by GaAs. [19, 20] However, compared with Si nanoarray structure, the research on GaAs nanoarray structure is relatively reported

For the preparation process of GaAs nanoarrays, researchers from the university of Illinois[21] presented a GaAs nanopillar array with soft lithography and metal-assisted chemical etching (MacEtch) process in the year of 2011. The fabricated nanostructures have uniform width which can be used in optoelectronic devices and optical detectors. The researchers from Chinese Academy of Science[19] analyzed the properties of GaAs nanoarray anti-reflection resistance through theoretical simulation with FDTD software, providing a detailed theoretical reference for the optical properties of nanostructures. In 2012, Yeeu-Chang Lee and his colleagues[22] prepared sub-micron nanoarray structures on GaAs substrate using colloidal crystal lithography barrier layer, which has been widely used in solar cells. In 2016, Yun won Song et. al[23] fabricated GaAs subwavelength structures by Au-assisted chemical etching. The fabricated GaAs structures dramatically reduced the total reflectance to 4.5% in a wavelength range of 200–850 nm up to the incident angle of 50°. In 2018, Paola Lova et al[24] demonstrated anisotropic metal assisted chemical etching of GaAs wafers exploiting the lower etching rate of the monoatomic Ga $\{111\}$ and $\{311\}$ planes. They also proposed a qualitative reaction mechanism for anisotropic etching of GaAs and show that reflectance of the roughened surface of black GaAs reduces up to ~ 50 times compared to polished wafers. In 2020, Paola Lova et al [25] proved that the etched GaAs (black

GaAs) presented satisfactory light trapping properties and the etched sample attracts more photon recycling. The articles mentioned above all proved that GaAs nanometer array structure has excellent photoelectric properties. But most of them were fabricated through metal assisted etching, which requires complicated chemical process and the disposal of waste liquid such as HF is also troublesome. Moreover, Au is used as the auxiliary metal, and the cost is relatively high.

So here we demonstrate a black GaAs fabrication process using a simple Inductively coupled plasma (ICP) etching process, and no extra lithography process, etc. The fabricated sample has a low Reflectance value, close to 0. Besides, the black GaAs also displayed hydrophobic property, with a water contact angle(CA) of 125°. On the whole, this kind of black GaAs etching process could be added to the fabrication workflow of photodetectors and solar cell devices to further improve their characteristics.

Method

2.1 Black GaAs nanoarrays fabrication process

All samples were cut into 1.5 cm × 2 cm pieces of bulk GaAs, the samples were pre-cleaned with conventional solvent and rinsed in deionized (DI) water. Then the experiments were performed in an Oxford System100 etching reaction chamber, equipped with a maximum available power 900 W, 13.56 MHz RF coil generator. The gases employed in this study were BCl₃, Cl₂, Ar, N₂ and O₂. During all the experiments, the temperature of the electrode was fixed at 25°C. A 5-min-long oxygen clean procedure was performed between each run to remove any polymer from the reactor sidewalls, minimize contamination, and preserve process repeatability. The samples were loaded into the reactor by mounting them on an SiO₂ carrier wafer, since the sample was etched at low temperature, silicone grease was unnecessary before etching process[26]. As part of the optimization of the etching parameters, different etching time for measuring the process outcome was employed, as shown in Fig. 1.

2.2 Characterization

Figure 1 showed SEM images of GaAs substrate under different etching time. From the picture we can see that etching depth increases with the increment of etching time, but the morphology of the sample does not change greatly. After etching, the surfaces of GaAs samples become flocculent, relatively uniform in height but scattered around. This kind of flocculent structure greatly increases the specific surface area of the device and can be applied in the fields of supercapacitors and sensors.

We also tested the reflectivity of the prepared structure with Agilent's Cary 7000 spectrophotometer and found that the flocculent structure of GaAs sample had a very low reflectivity, as shown in Fig. 2. In the wavelength range of 590–800 nm, the reflectivity is 3 min < 5 min < 4 min. In the wavelength range of 400–590 nm, the reflectivity is 5 min < 4 min < 3 min. In the meantime, we can see that the reflectivity of the samples under different etching time is very low, with a difference of less than 1%. Considering the time and cost in the actual process, we choose 3 min as the fixed etching time in the subsequent experiments. We attribute the decrement of reflectivity to the rough structure formed on the GaAs surface.

The sample formed a cluster structure after etching and the roughened surface will limit the reflection of light and reduce the scattering of light, thus reducing the reflectivity of light. To verify our conclusion, AFM images were performed on the surface of the etched sample and the unetched sample, as shown in Fig. 3. The results show that the surface roughness of the etched sample is much larger than that of the unetched sample.

Then we investigate the effect of etching gas flow rate on the surface morphology and reflectivity of the sample when etching time is fixed at 3 min, and the oxygen flow was controlled. Here the role of oxygen is to form oxides during the etching process, and because of the different volatilization temperatures during etching process, oxygen reacts with base atoms to form a micro-mask, thus affecting the etching result. Here, the oxygen flow ratio is set as 2:3:4, and the SEM images after etching are shown in Fig. 4. It can be seen from the figure that when the oxygen flow ratio is 3, the etched GaAs surface presents a neat columnar shape, while when the oxygen flow ratio increases to 4, the GaAs surface becomes bright, and the sample surface is found to be smooth and without any pattern, as shown in Fig. 4c. The main reason for this phenomenon is that as the increment of oxygen flow, the etching rate will be accelerated. When the oxygen flow increases to a certain extent, the structure formed during etching process on the substrate surface will be etched away, thus obtaining the sample shown in Fig. 4c. Cary7000 spectrophotometer was used to test the reflectivity of the three samples with different morphometry, and we found that the reflectivity increased gradually with the increase of oxygen flow. When the oxygen flow ratio is 2, the reflectivity is extremely low, nearly close to 0 within the GaAs absorption range, as shown in Fig. 5. This low reflectivity is caused by the excessive oxygen flow. Sufficient oxygen oxidized the surface structure formed by previous etching and made the surface of the sample smooth and flat, as shown in Fig. 4c. The etched sample with smooth surface presented high reflectivity. When the oxygen flow ratio is 2, the etched samples has the lowest reflectivity, because the flocculent surface of black GaAs greatly increase the propagation path of photons and reduce the reflection of light. The structured GaAs sample also presented hydrophobicity, while the contact angle is 125° , as shown in the enlarged SEM images of Fig. 4(d), broadening the application range of black GaAs.

Conclusions

In summary, we demonstrated a lithography-free ICP etching process for structuring GaAs surfaces with near-zero reflection (black GaAs). The structured sample displayed superior antireflective properties, yielding reflectance values as low as 0.093. The microstructures were obtained by only one step ICP etching process, and can be prepared in large scales. Moreover, the black GaAs sample presented hydrophobic property as the contact angle is 125° . This kind of structure is anticipated to absorb photon efficiently and reduce photon loss associated with light emission during charge recombination. The related preparation process also provides more possibilities for the preparation and development of GaAs devices.

Abbreviations

ICP

Inductively coupled plasma; CA:contact angle; LEDs:light emitting diodes; PV:photovoltaics; FETs:field effect transistors; MacEtch:metal-assisted chemical etching; DI:deionized; SEM:Scanning electron microscopy; AFM:Atomic Force Microscopy.

Declarations

Availability of Data and Materials:

All data generated or analyzed during this study are included in this published article.

Competing Interests:

The authors declare no conflict of interest.

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Author Contributions:

JM and XDW wrote the paper; YQZ analyzed data and revised the manuscript; WL helped performing the analysis and discussion; XDW and FHY guided the project. All of the authors have discussed the results and approved the submitted version.

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Figures

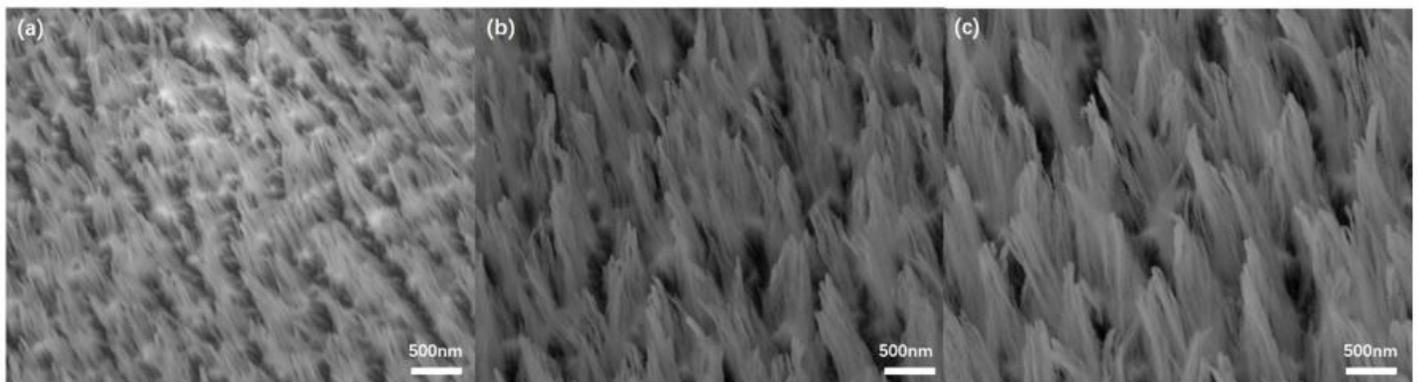


Figure 1

SEM images of GaAs substrate under different etching time. (a) 3 min; (b) 4min; (c) 5min.

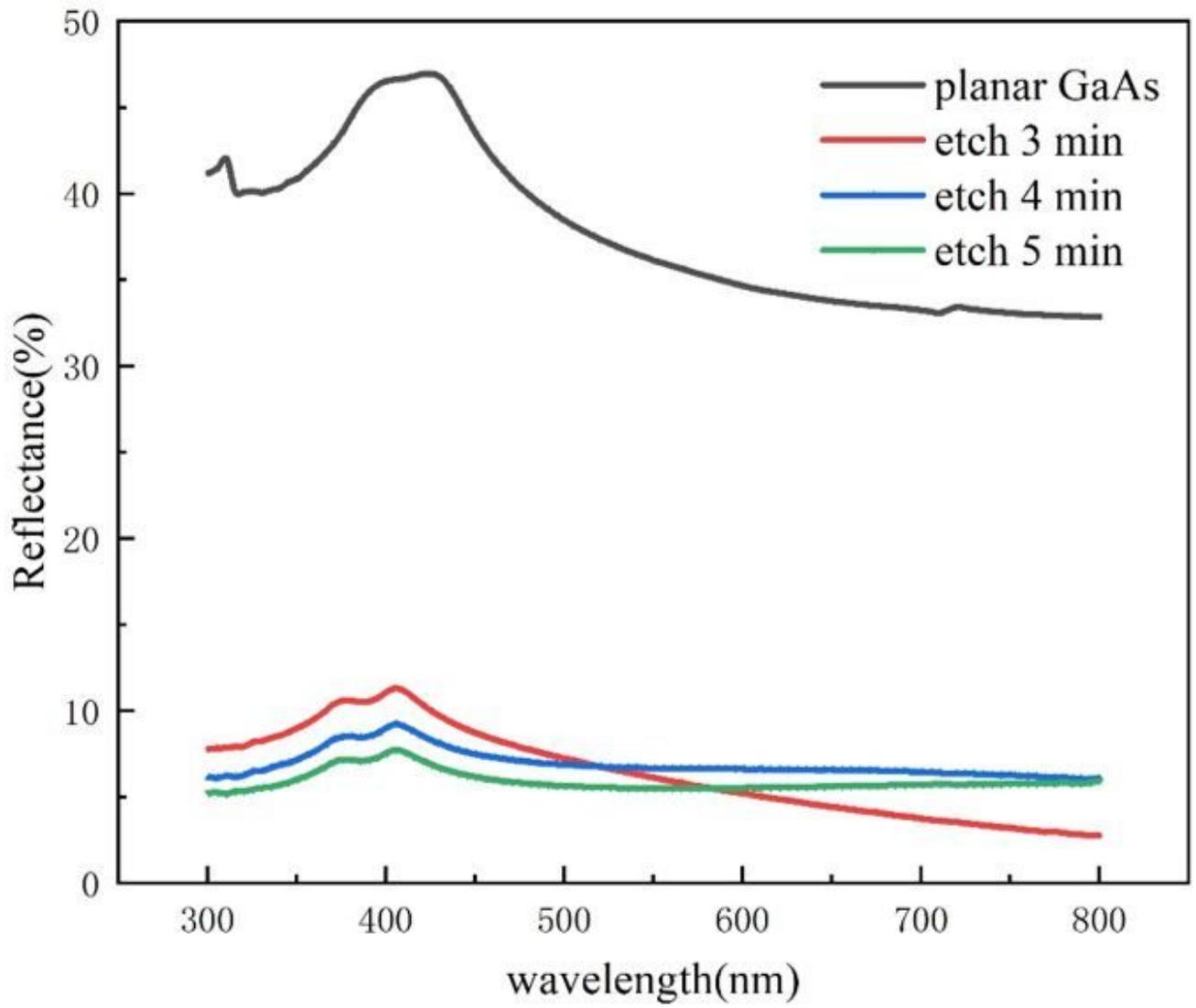


Figure 2

Reflectance of GaAs substrate under different etching time.

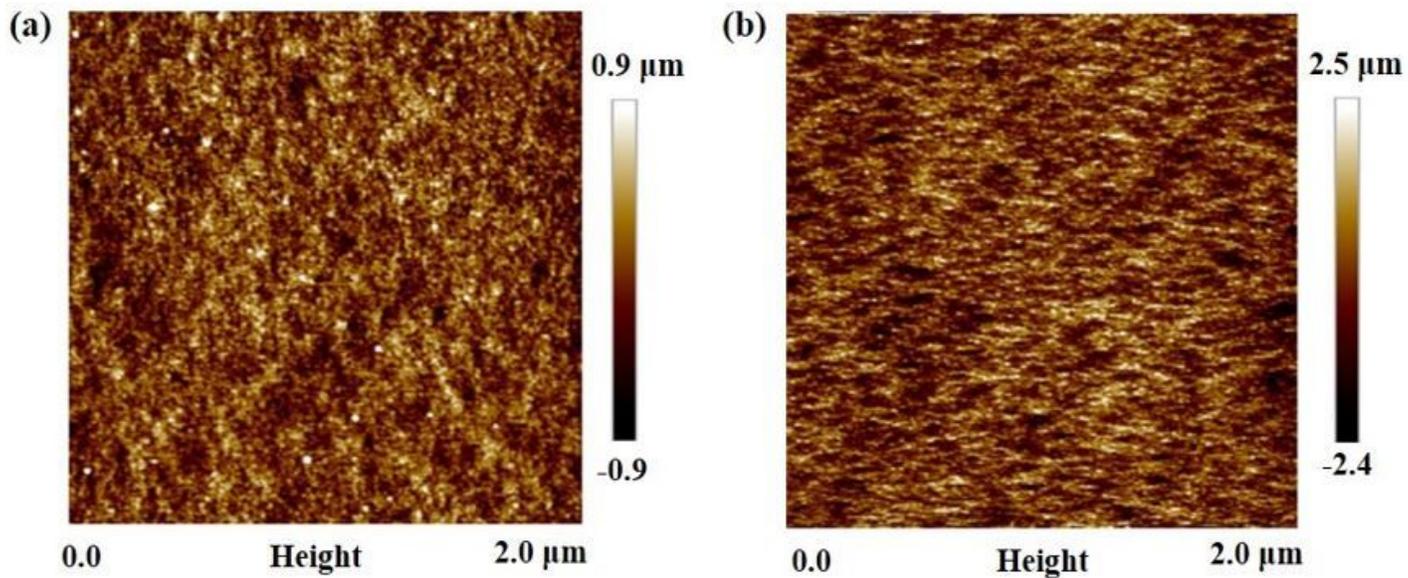


Figure 3

AFM images of (a) unetched GaAs sample; (b) black GaAs.

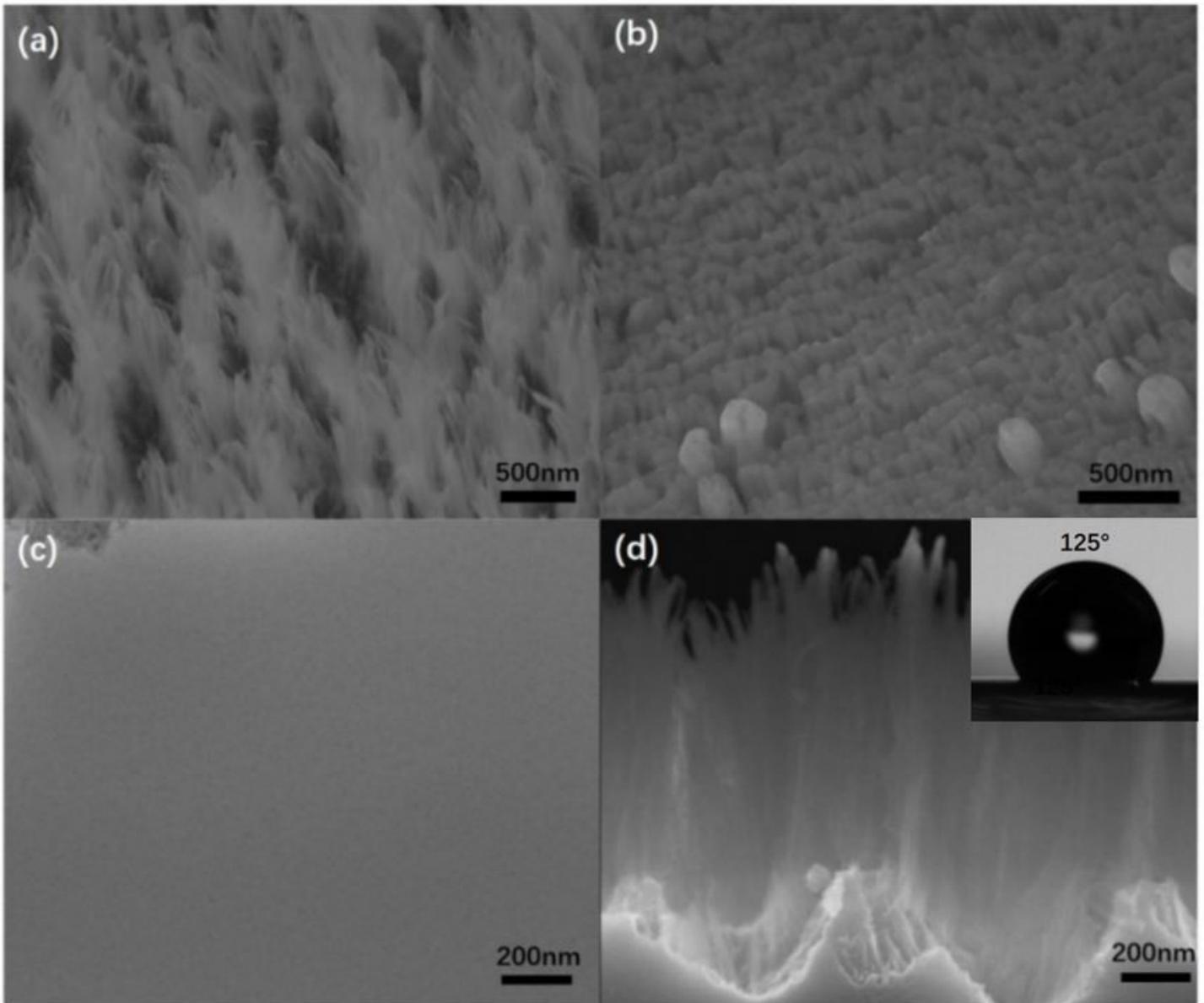


Figure 4

(a-c) SEM images of GaAs substrate under different oxygen flow rate; (d) the cross-section SEM image of GaAs substrate under the oxygen flow rate of 2.

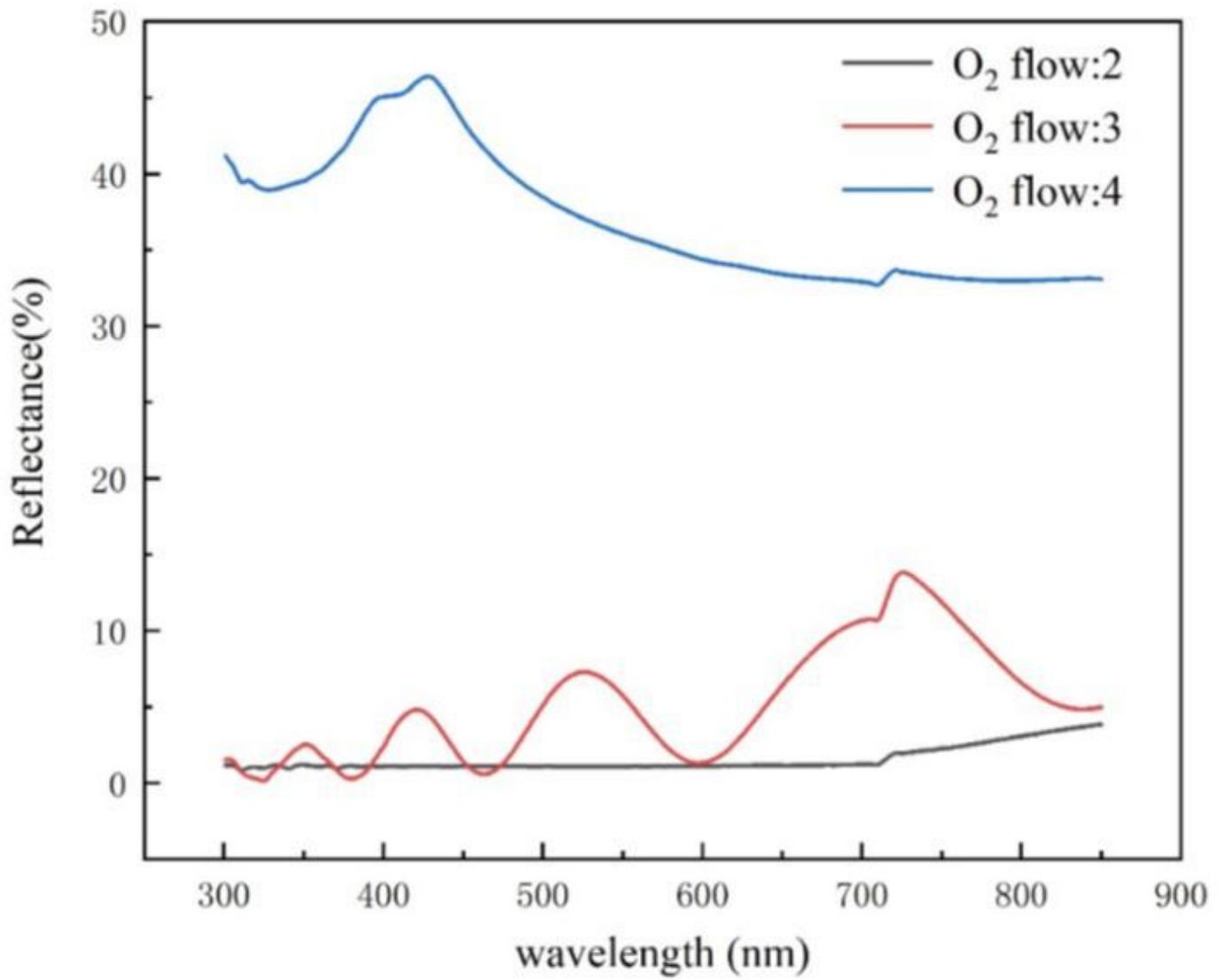


Figure 5

Reflectance of GaAs substrate under different oxygen flow rate.